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Title:	PEM Fuel Cell Catalyst Layer Structure Degradation During Carbon Corrosion
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PEM Fuel Cell Catalyst Layer Structure Degradation During Carbon Corrosion

Electrochemical Society

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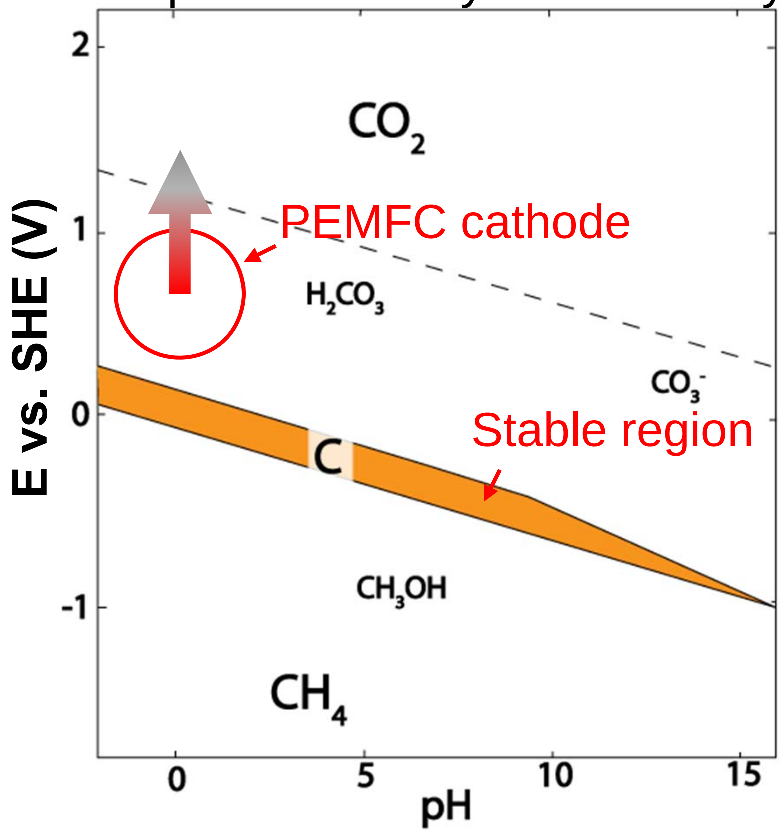
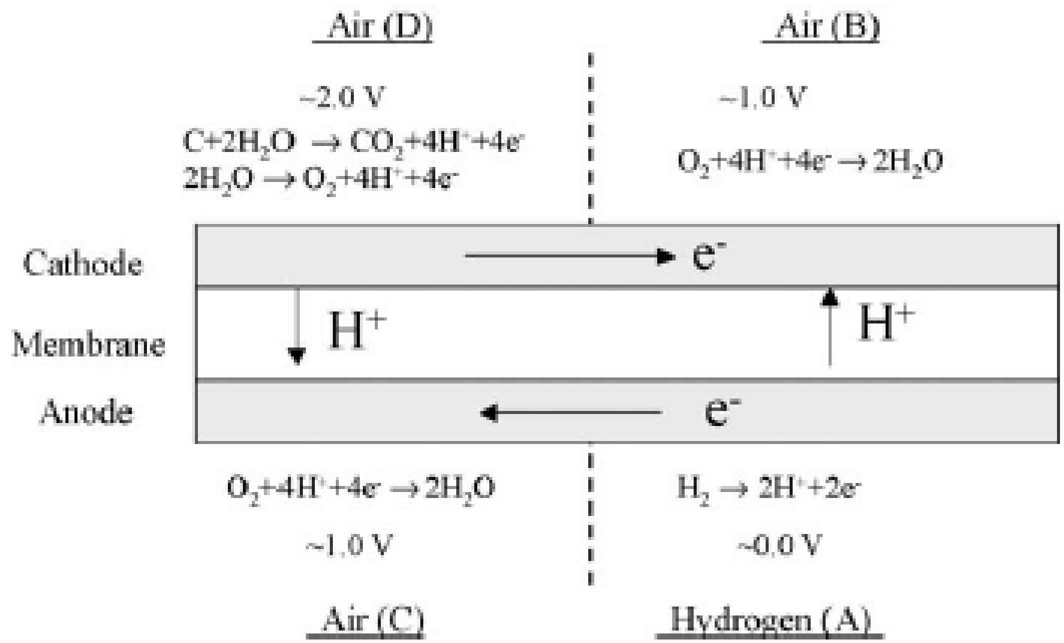
Carbon in the PEMFC environment

Graphite thermodynamic stability



Adapted from M. Pourbaix, *Atlas of Electrochemical Equilibria* (1966)

Regional reversals raise potentials dramatically



C.A. Reiser et al, *Echem & SS Lett.* (2005)

Figure from H. Tang et al, *J. Power Sources* (2006)

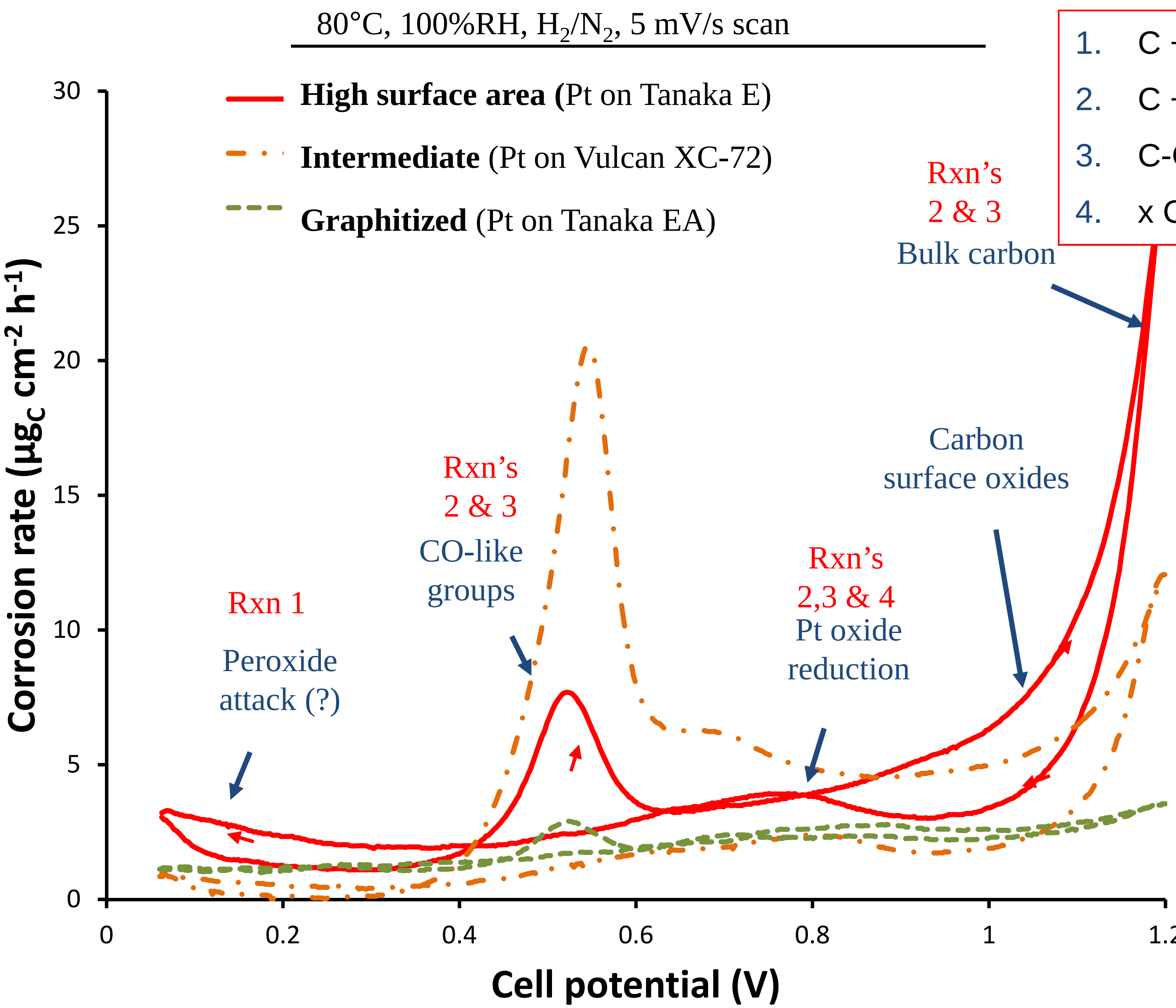
Approach

- Time Effect of Electrode Structure Change
  - Quantify carbon corrosion and correlate with durability and performance
- **US DOE Fuel Cell Tech Team drive cycle:**
  - After conditioning
  - 100 hours, 200 hours, ….
- **Carbon corrosion AST (Accelerated Stress Test)**
  - 20% Pt/HSAC (E - High Surface Area Carbon) – 1.2V hold vs time
  - 20% Pt/Vulcan (V)
  - 20% Pt/LSAC (EA - Low Surface Area Carbon)
- **Characterization Methods to Correlate Electrode Structure to Durability**
  - VIR, Impedance, CO_2 Production, SEM, TEM and HAADF-STEM analysis
- **Modeling**
  - Integrated degradation model – kinetic/rate based (ANL)

Carbon Corrosion in MEAs: CO_2 Production

High Surface Area (E), Intermediate (V), Low (graphitized - EA)

1. $C + H_2O_2 \rightarrow CO_2 + 2\,H^+ + 2e^-$
2. $C + H_2O \leftrightarrow C\text{-}O + 2\,H^+ + 2e^-$
3. $C\text{-}O + H_2O \rightarrow CO_2 + 2\,H^+ + 2e^-$
4. $x\,C + H_2O \leftrightarrow C_x\text{-}O + 2\,H^+ + 2e^-$

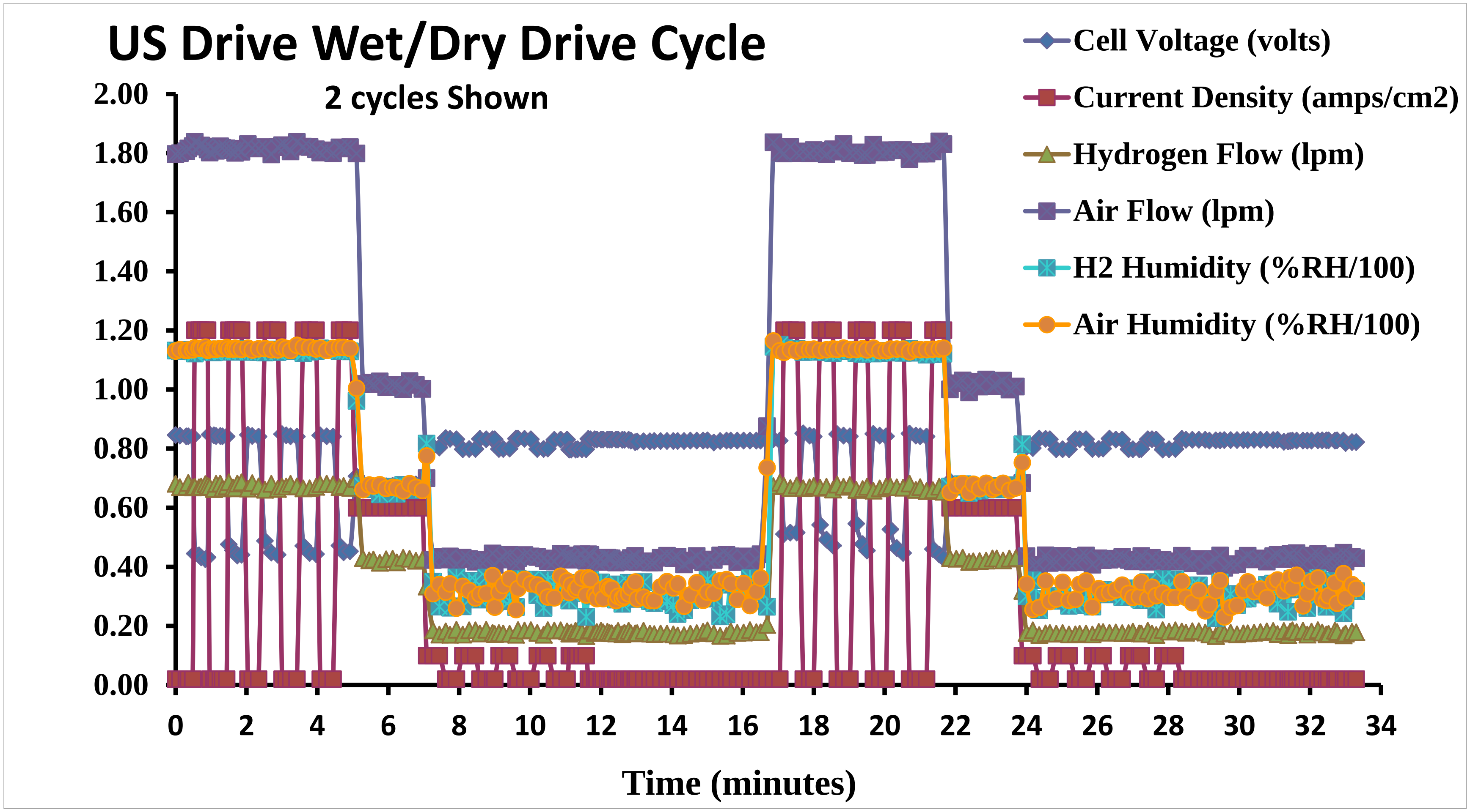


Pt catalyzed corrosion of Ketjen black (E-type), Vulcan XC-72 (V-type) and graphitized carbon (EA-type) supports

- Related Peak I to corrosion by peroxide
- Peak II to surface coverage by active oxides
- Peaks III and IV and hysteresis to Pt and surface coverage by passive oxides

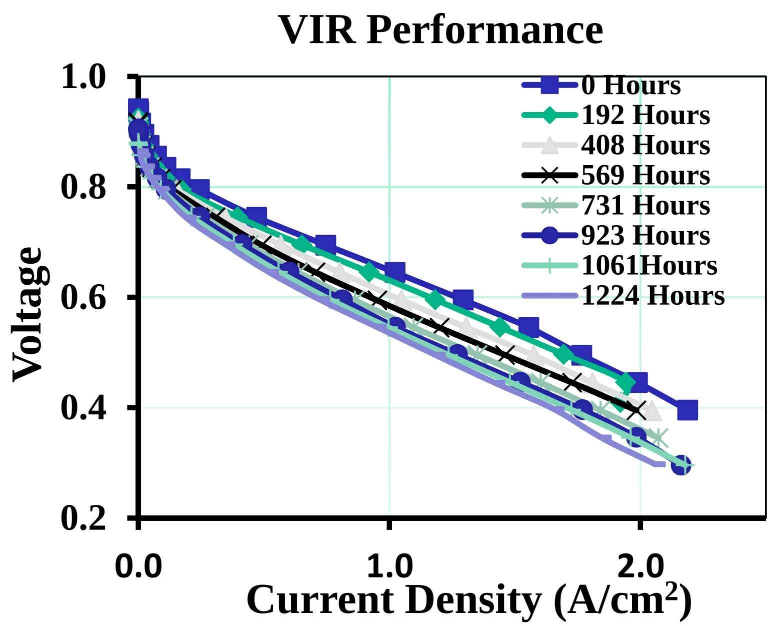
CO2 Measured by NDIR

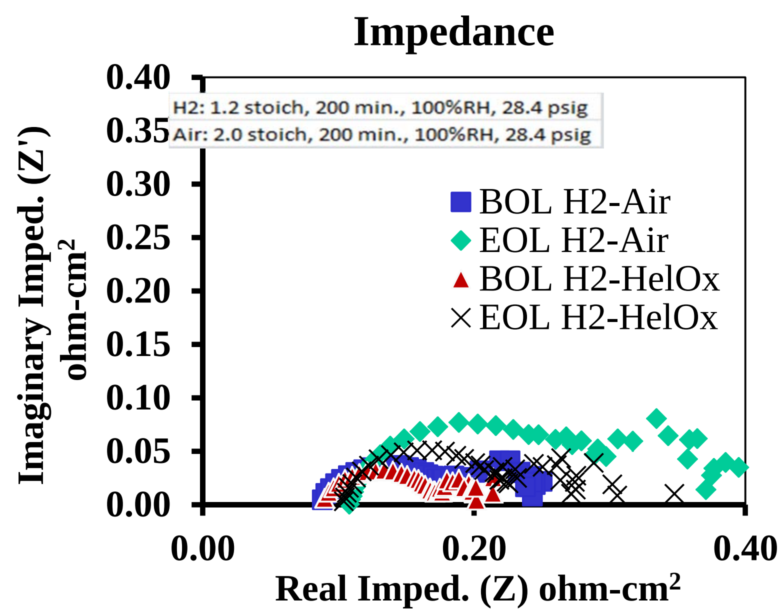
Drive Cycle Testing
(from U.S. Drive/DOE Fuel Cell Tech Team)

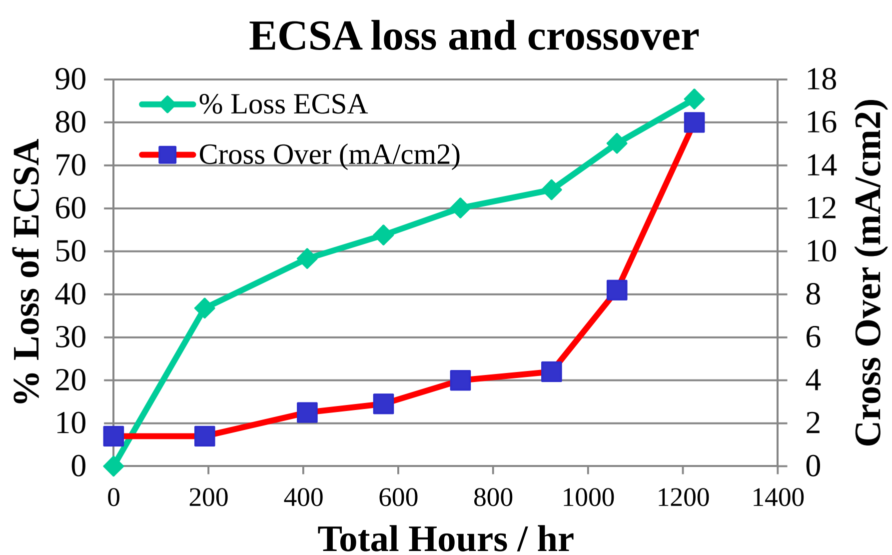


- Use 100% H_2 instead of 80% H_2
- One fuel cell test station capable of transient RH control
- LANL performing Wet/Dry Drive Cycles
- LANL performing Wet Drive Cycles

Performance During Drive Cycle Testing



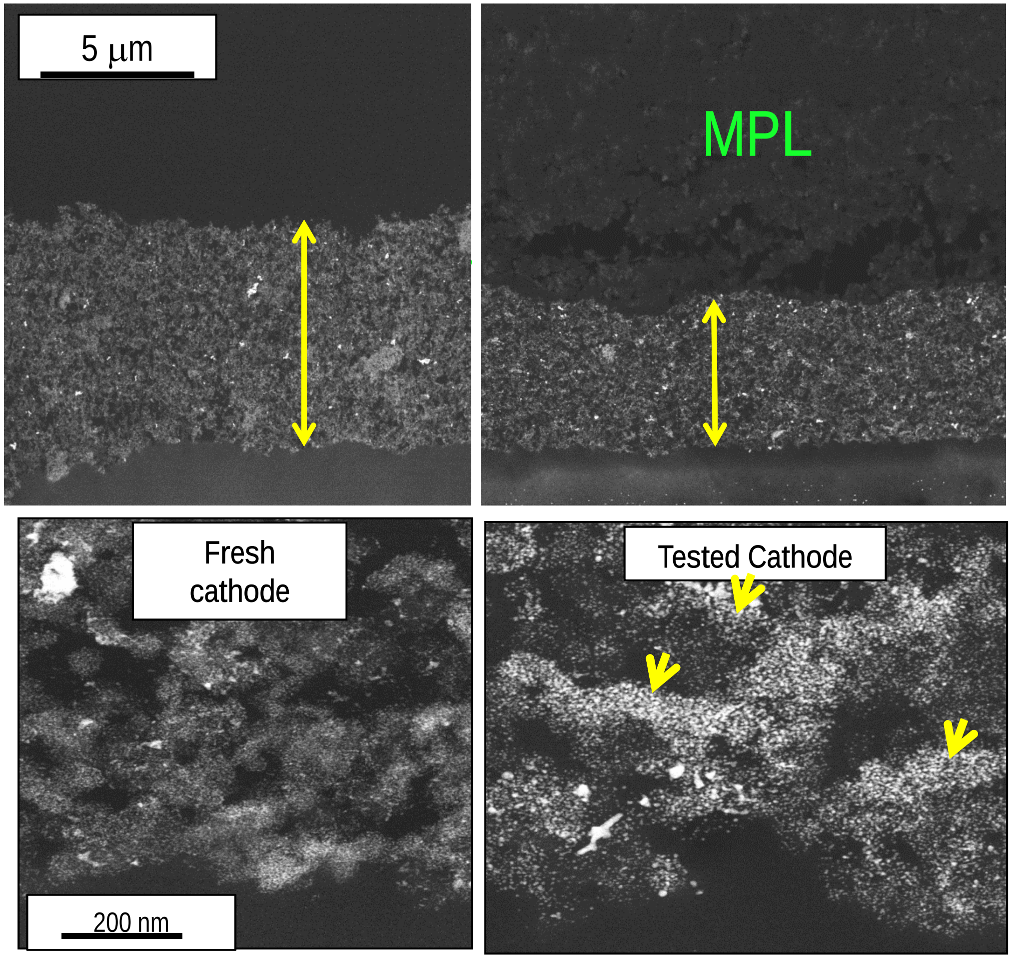




- Decreasing performance in both Kinetic and MT regions
- Small increase in the High Frequency Resistance
- Loss of ECSA
- Slow increasing gas cross-over, followed by larger
- Increasing Mass Transport resistance

Microscopic Characterization of Degradation After DOE/FC Tech Team Drive Cycle

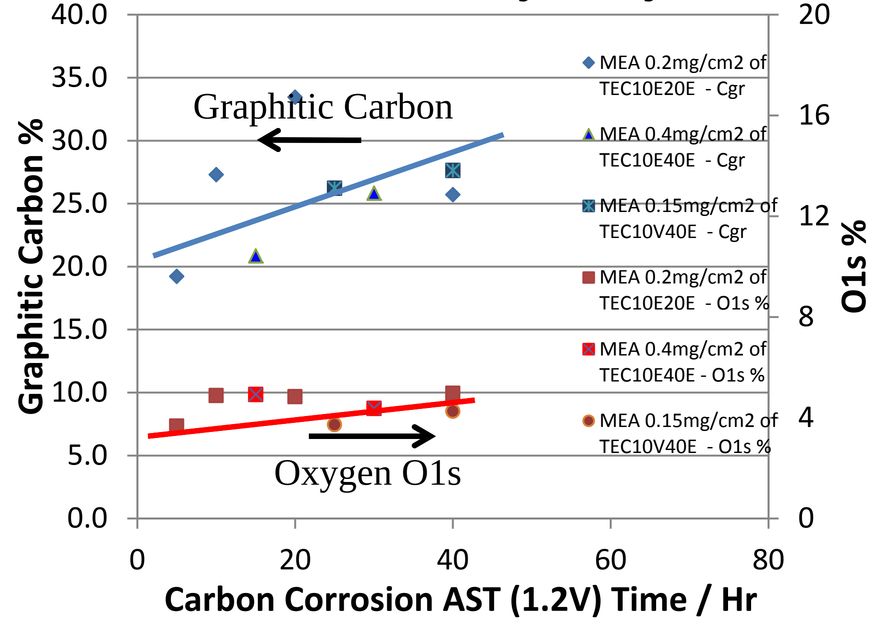
Fresh cathode | Tested cathode (300 hrs)



~30% compression/thinning of cathode layer due to localized effects

HAADF-STEM images

Elemental Analysis by XPS

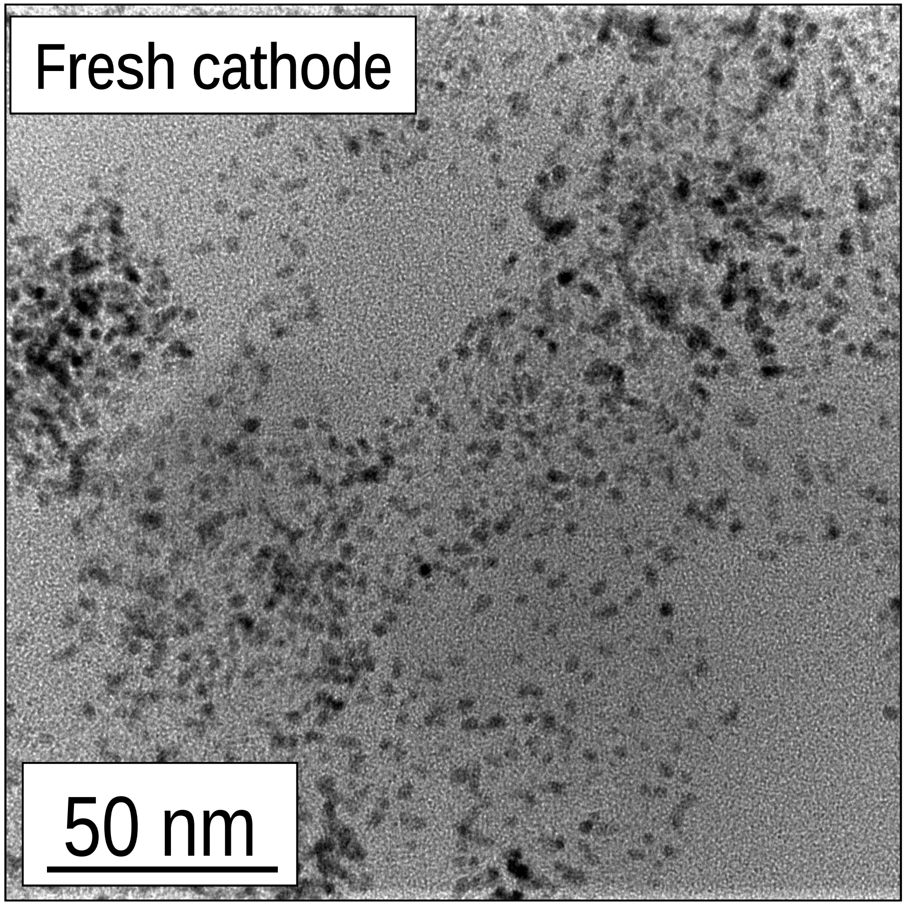


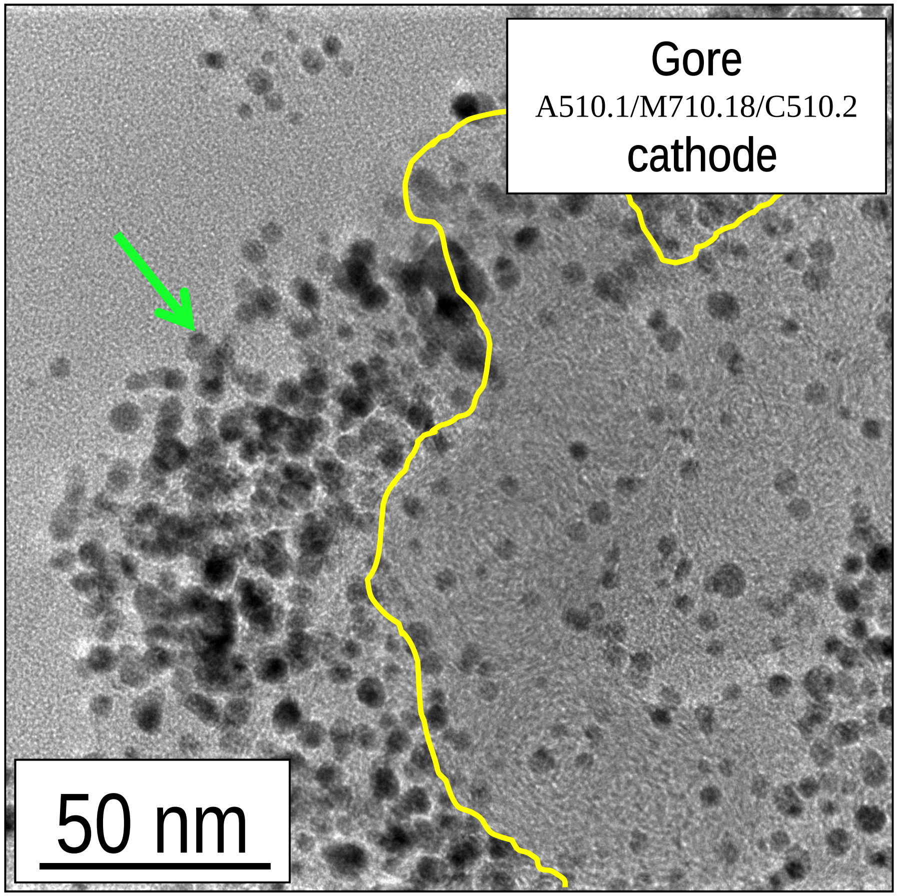
Ion Power MEAs with different carbon support

- Graphitic content increases (as %)
  - Likely → decrease of amorphous carbon
- Oxygen content increases
  - Likely → increasing oxygen content on carbon surface
  - Changing hydrophobicity effects transport

Gore "fresh" vs. Drive Cycle Tested (303 hr wet/dry drive cycle)

Microscopic Characterization of Carbon Corrosion
(After DOE Drive Cycle Test – 300 hrs)

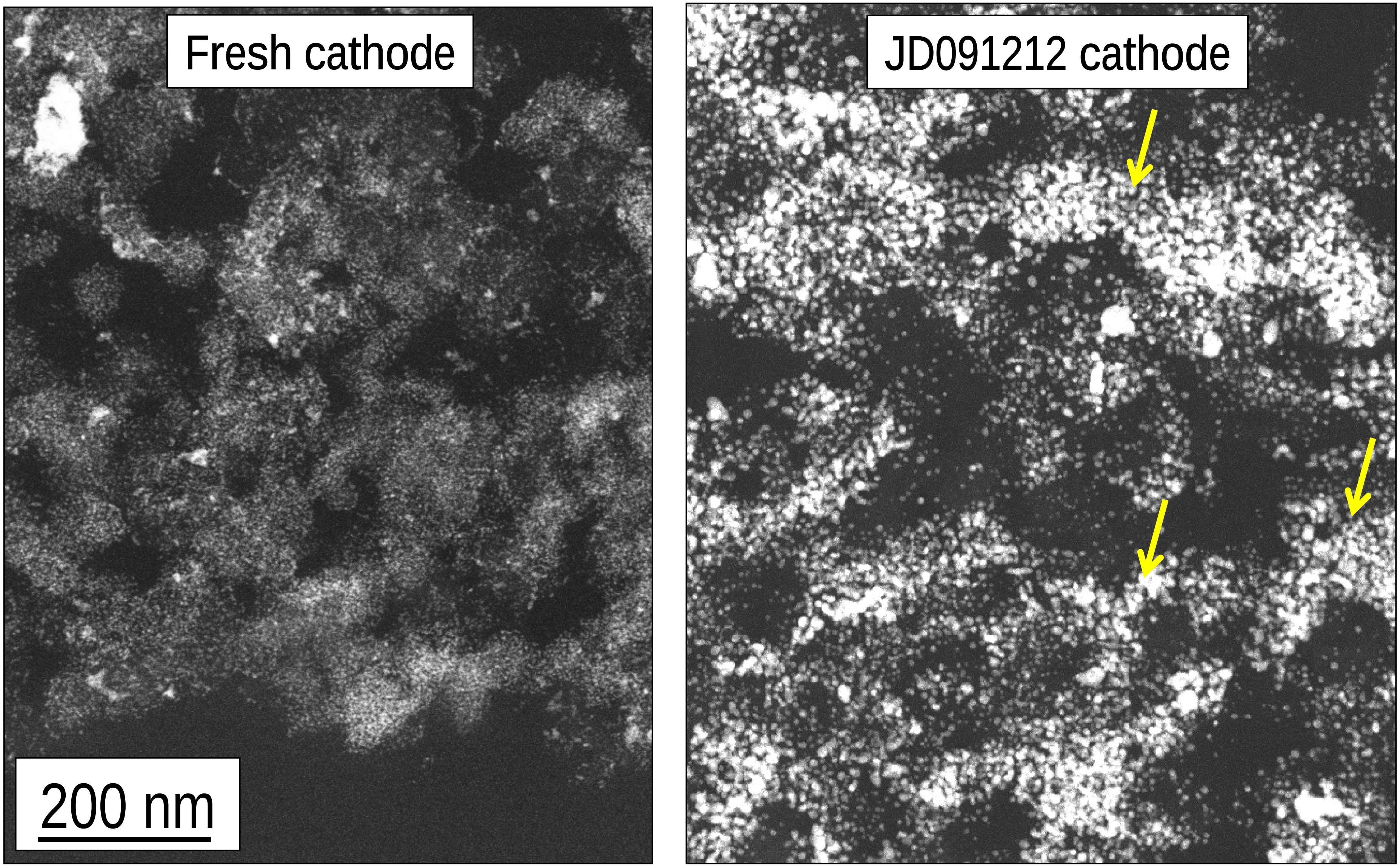




- "localized bands" of HSAC corrosion (green arrows), which are correlated increased Pt particle sizes and closer Pt-Pt interparticle spacings. Typically, these oxidized regions of carbon surround non-oxidized regions (inside yellow outline).
- Regions of non-oxidized HSAC retain graphitic structure and are correlated with smaller Pt particle sizes

TEM images

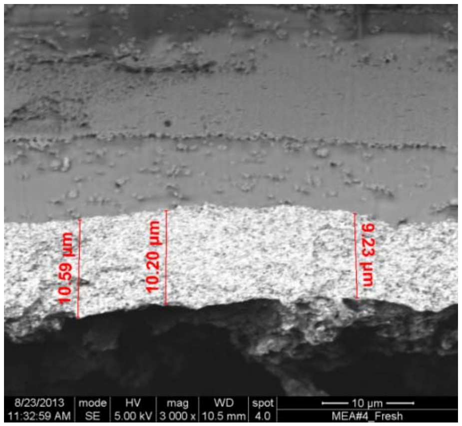
Fresh vs. Aged (1224 hr wet drive cycle)



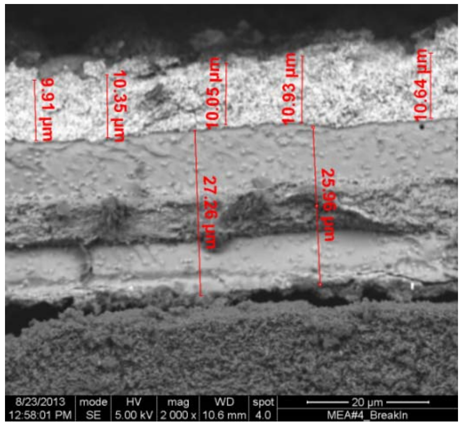
"localized bands" of HSAC corrosion observed, which are correlated with regions of increased Pt particle sizes and closer Pt-Pt interparticle spacings (yellow arrows)

Fast Catalyst Layer Thickness Change during Drive Cycle Operation - MEAs: Ion Power (Vulcan Carbon)

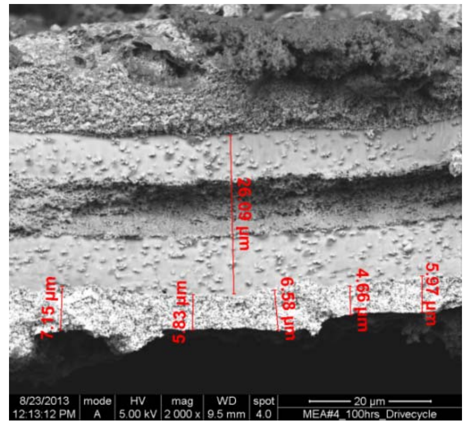
SEM Comparison over testing time



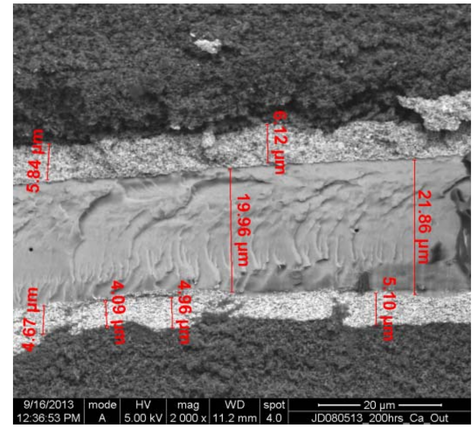
Fresh
9 microns



Conditioned
9 microns



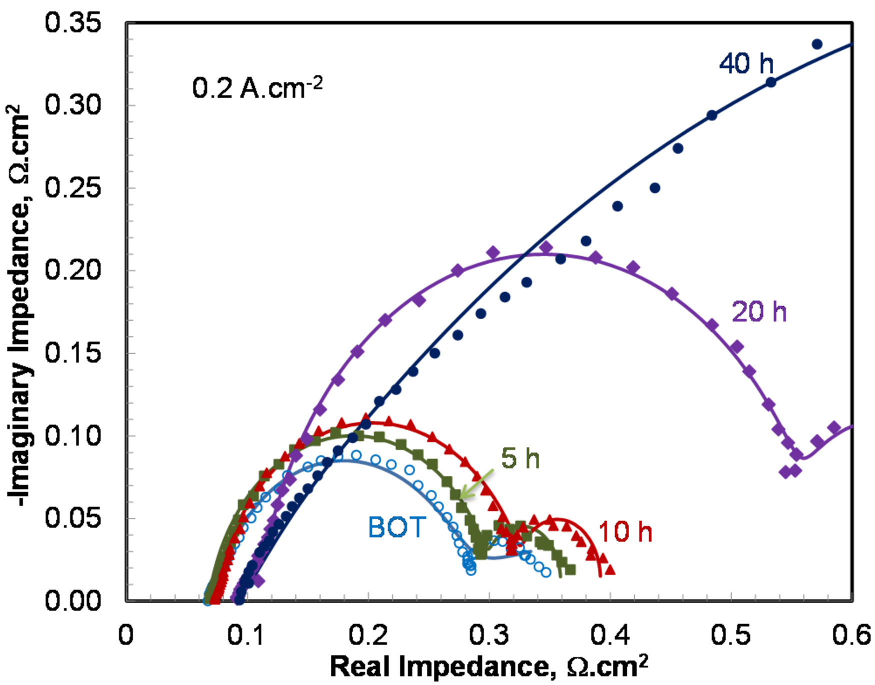
100 hrs
6 microns

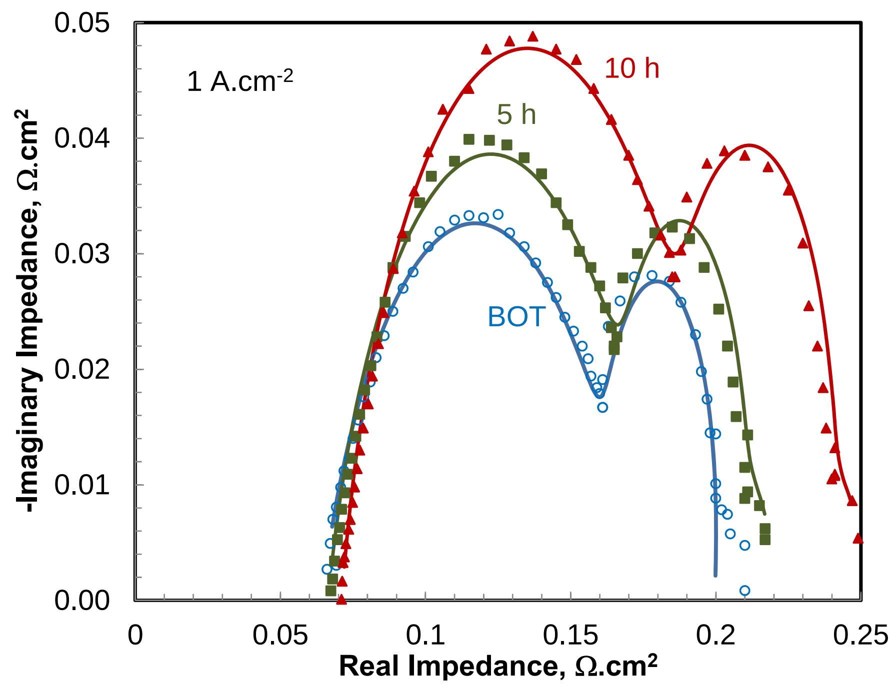


200 hrs
5 microns

- Significant change in catalyst layer thickness over short period of time
- Without high potential operation (no shut-down/start-up)
- Carbon corrosion? Loss of 33% of carbon in 100 hours doesn't correlate with other measurements
- → Catalyst layer compaction

Mass Transport Analysis by Impedance





- Significant increase in mass transport losses
- Observe Catalyst layer thinning
- Large increase in MT losses from 10 hrs to 20 hrs

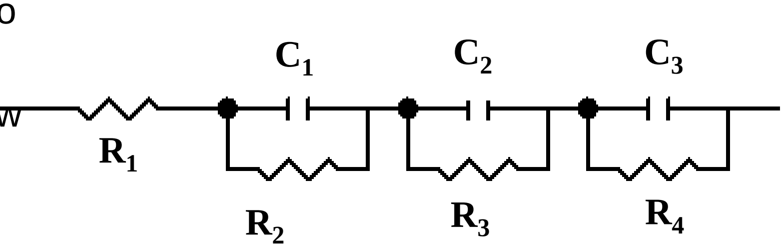
R_1: HFR including contact resistances

R_2: Resistance due to: ORR kinetics + proton conduction in cathode catalyst layer (CCL) + O_2 diffusion across ionomer to TPB*

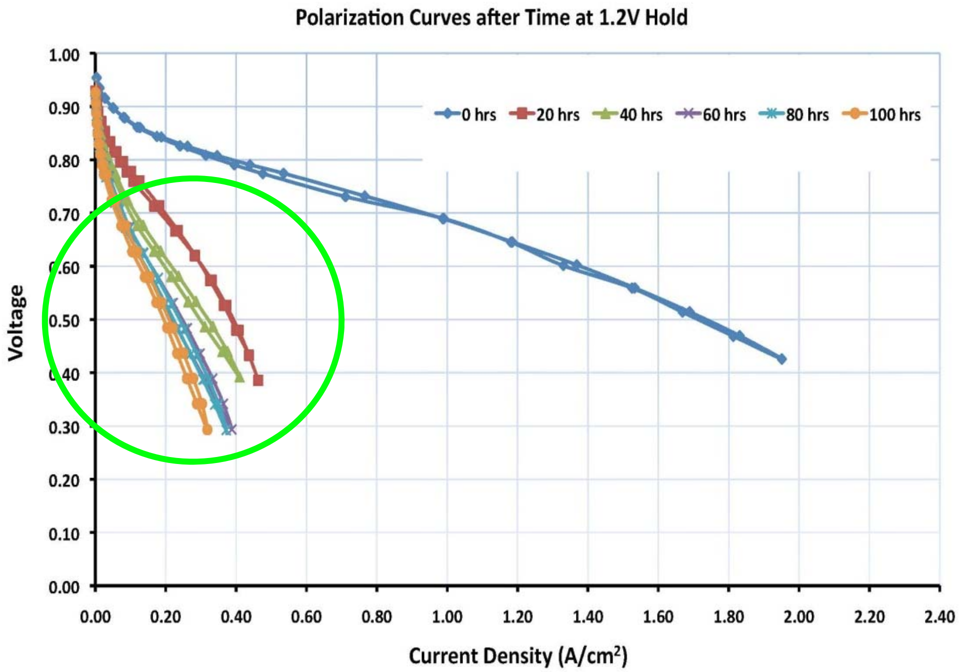
R_3: Resistance due to O_2 diffusion in CCL pores (and GDL + flow field)

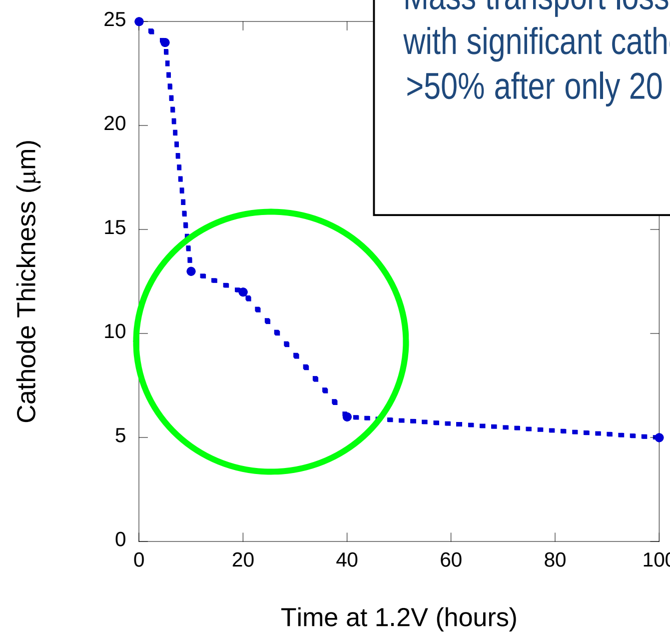
R_4: Resistance due to O_2 diffusion across GDL (and flow field)

ZVIEW Equivalent Circuit

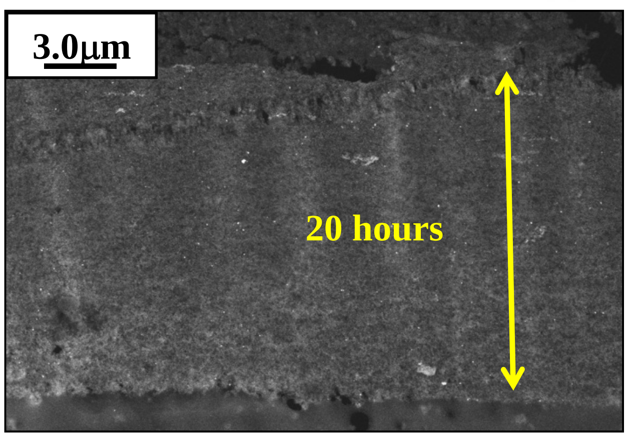


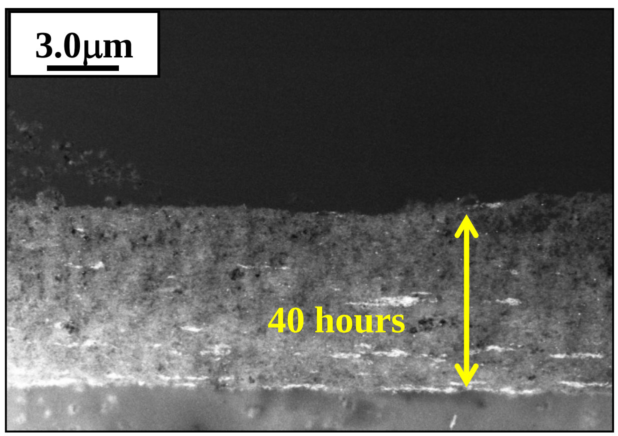
Effect of Cathode Carbon Corrosion on MEA Performance During AST (1.2 V hold)

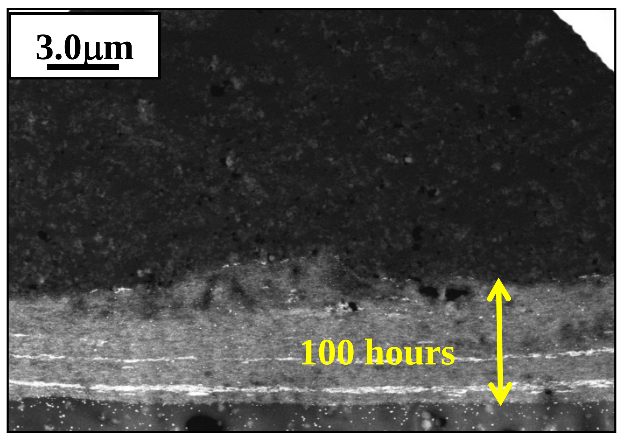




Mass transport losses associated with significant cathode "thinning" >50% after only 20 hours at 1.2V







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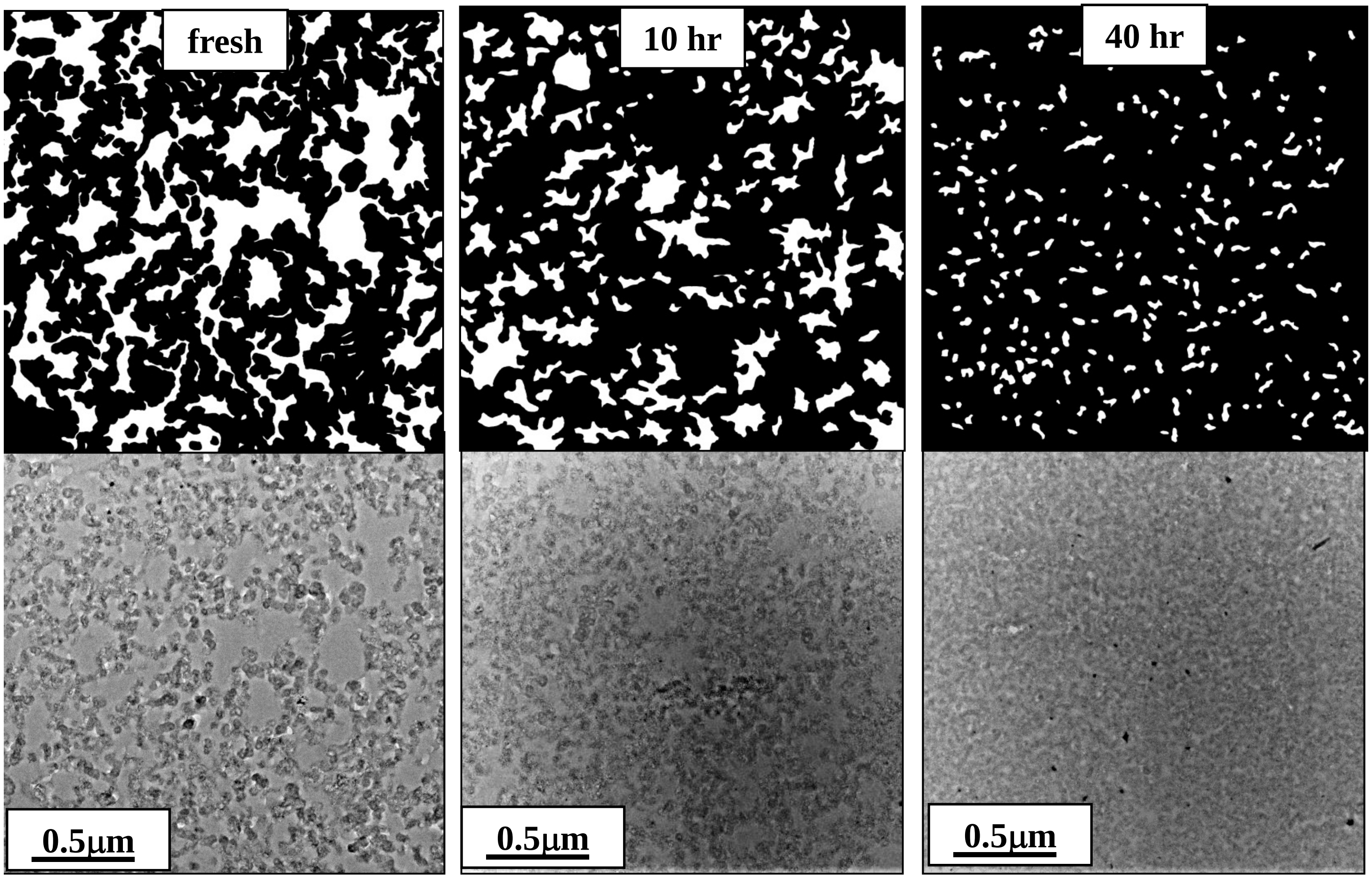
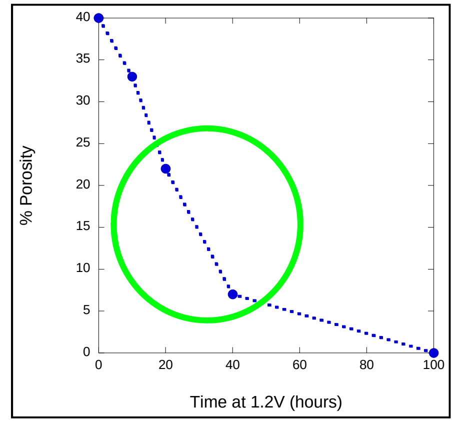
Cathode Carbon Corrosion Leads to Loss of Porosity





After 20h at 1.2V ~50% porosity loss in cathode layer

Binary images represent pore distributions after AST

Factors contributing to cathode thinning

- *loss or change in porosity*
- carbon oxidation – CO_2 evolution
- carbon oxidation – graphite oxide formation

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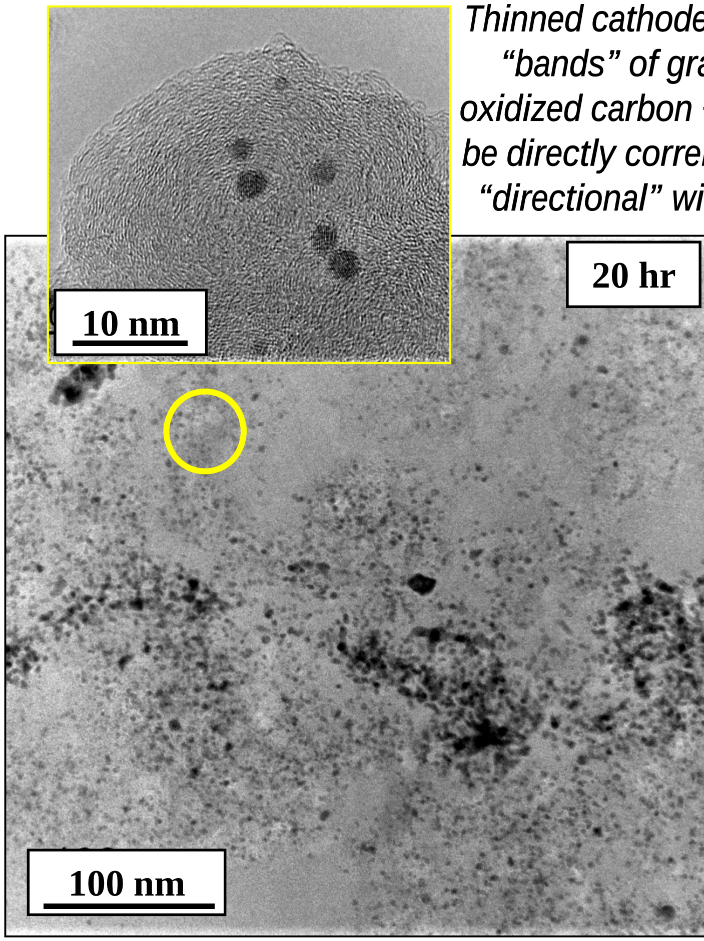
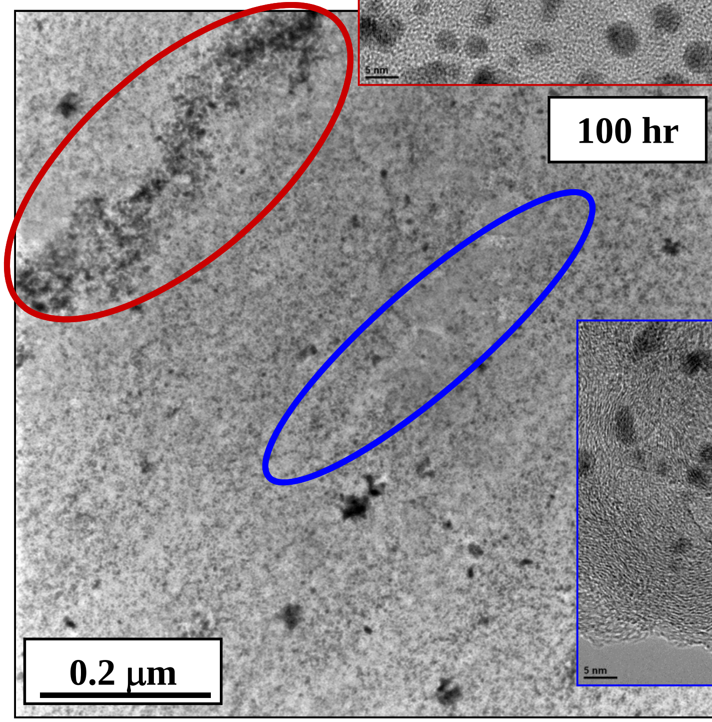
Carbon Corrosion Converts Carbon to Graphite Oxide

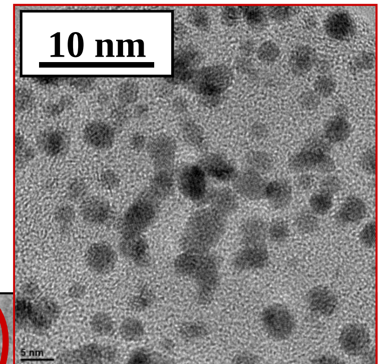
Factors contributing to cathode thinning
- loss or change in porosity
- *carbon oxidation – CO_2 evolution*
- *carbon oxidation – graphite oxide formation*

… but loss of porosity loss does not directly correlate with either CO_2 evolution or amount of oxidized carbon formed in cathode layer!

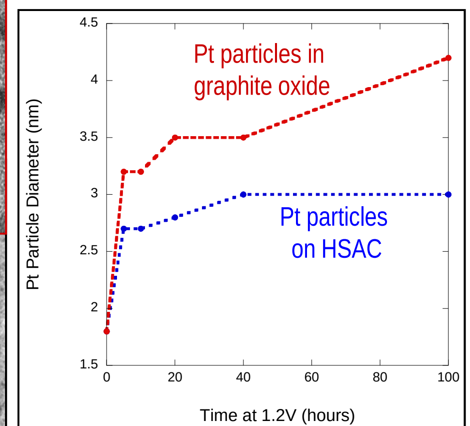
Thinned cathode is a layered structure of "bands" of graphite oxide + partially oxidized carbon + retained HSAC that can be directly correlated with Pt size and are "directional" with respect to membrane

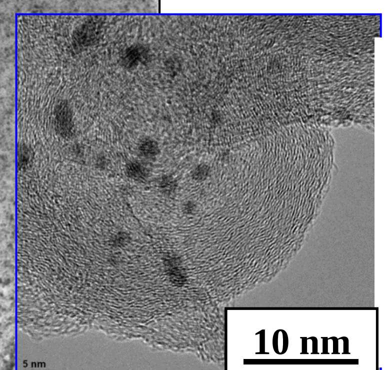






After 100 hr at 1.2V, much of the HSAC has been oxidized to form graphite oxide





After 100 hr at 1.2V, evidence for retained meso-graphitic HSAC structure

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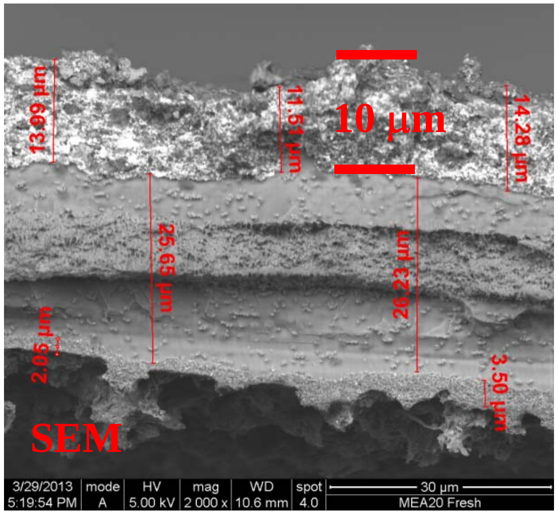
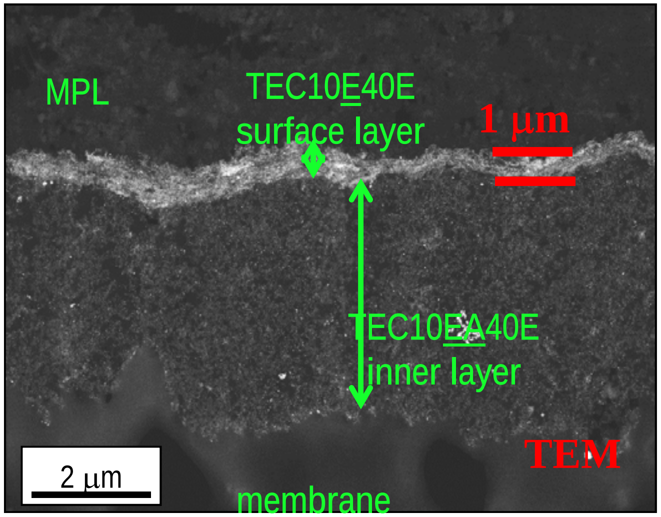
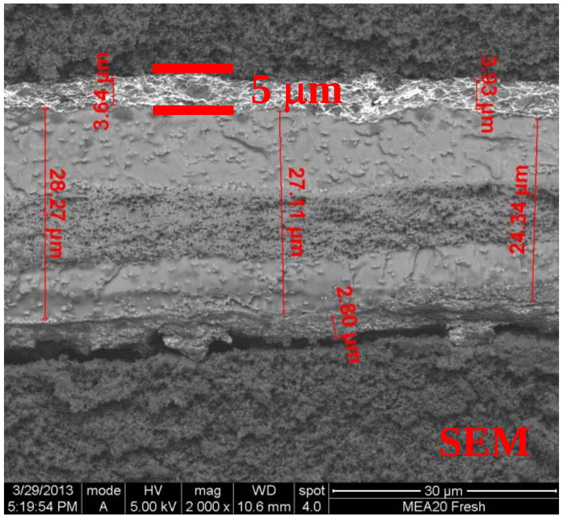
Comparison of Carbon Corrosion – Potential Mitigation of Transport Losses

Mixing Carbon Support Materials to Keep CL Structure and Activity

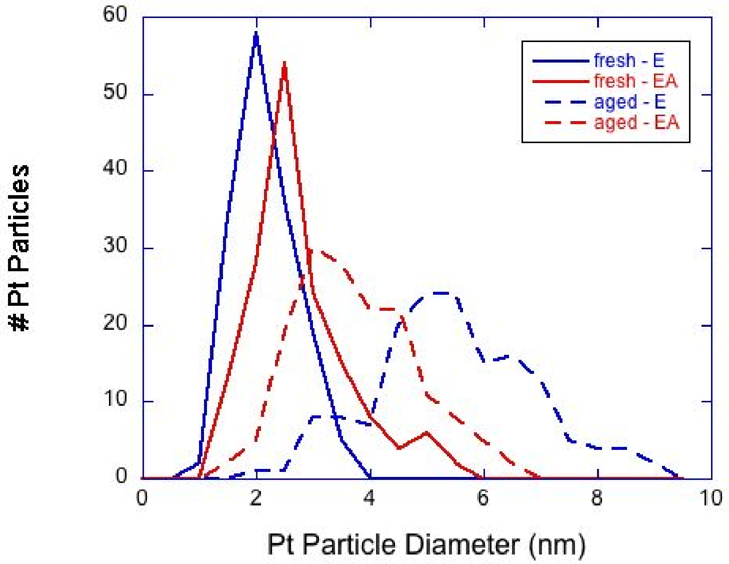
Fresh MEA (Ea) | **Tested MEA (E)** | **Tested MEA (Ea+E)**







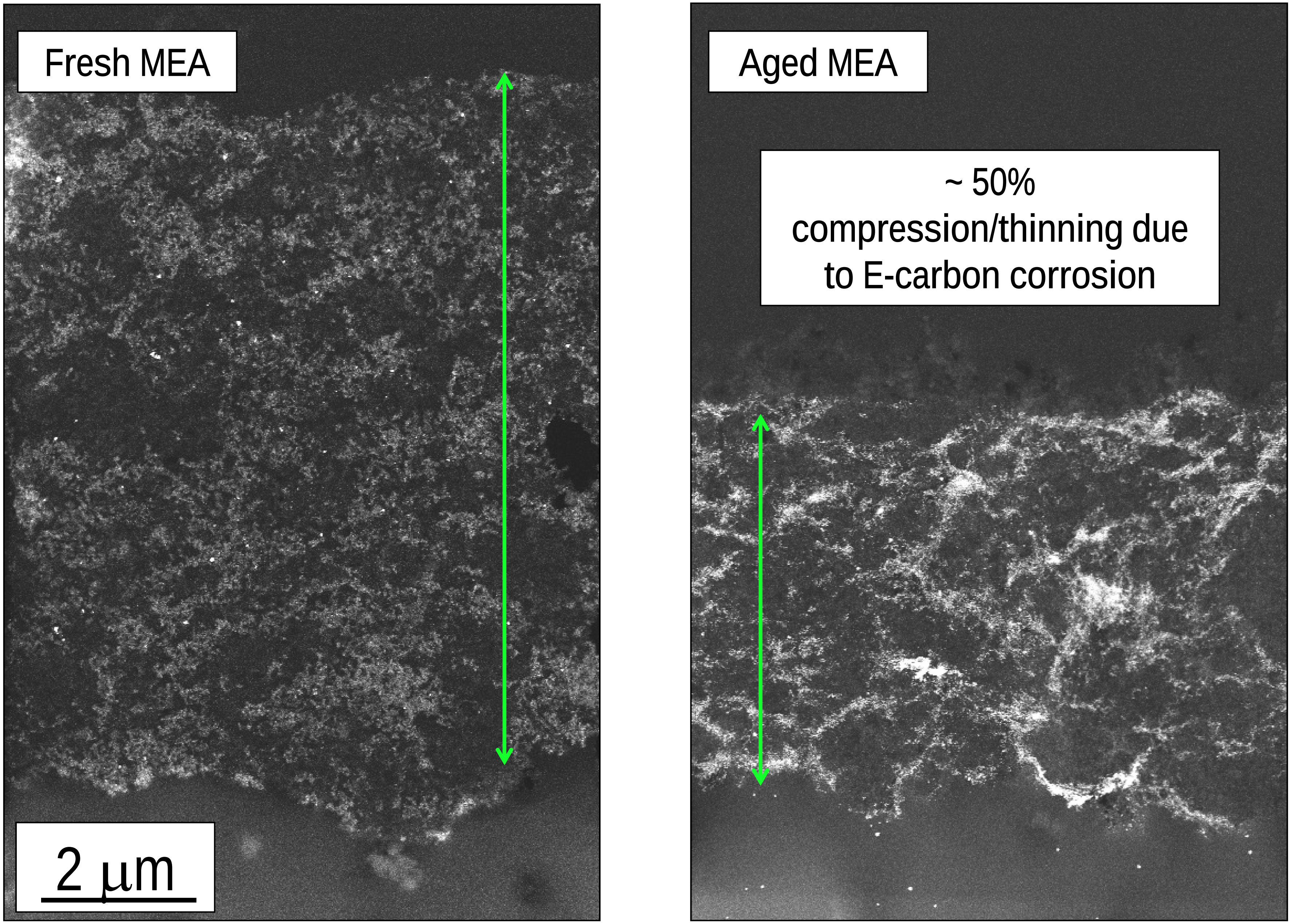
- **High Surface Area Carbon shows 10x decrease in CL thickness ~ 1 µm after test**
- **Mixed with graphitized carbon shows ~ 50% decrease in CL thickness**
  - **Keeps porosity available for transport**
- **Pt particle size growth observed for both types of carbon**



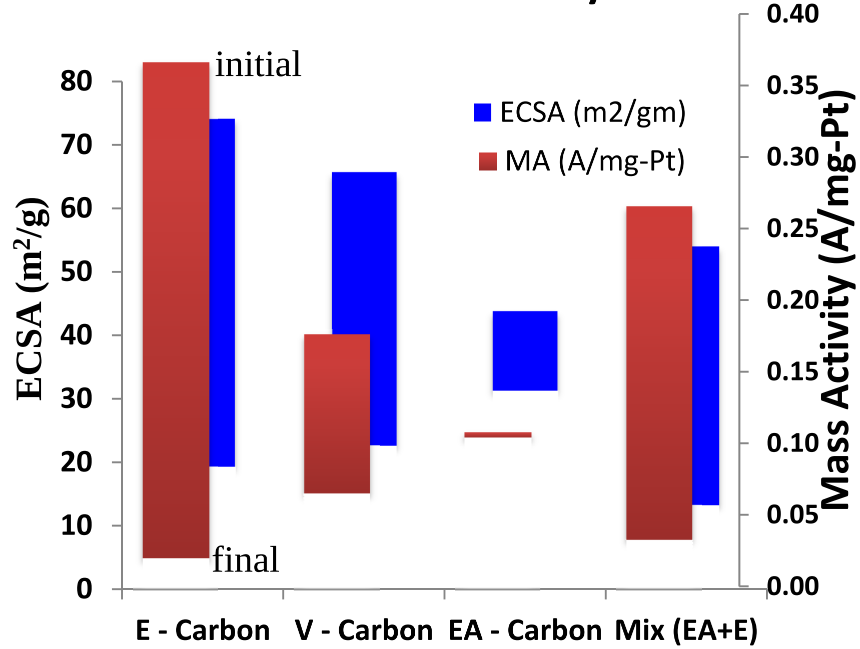
Carbon Corrosion AST – 1.2 V potential hold

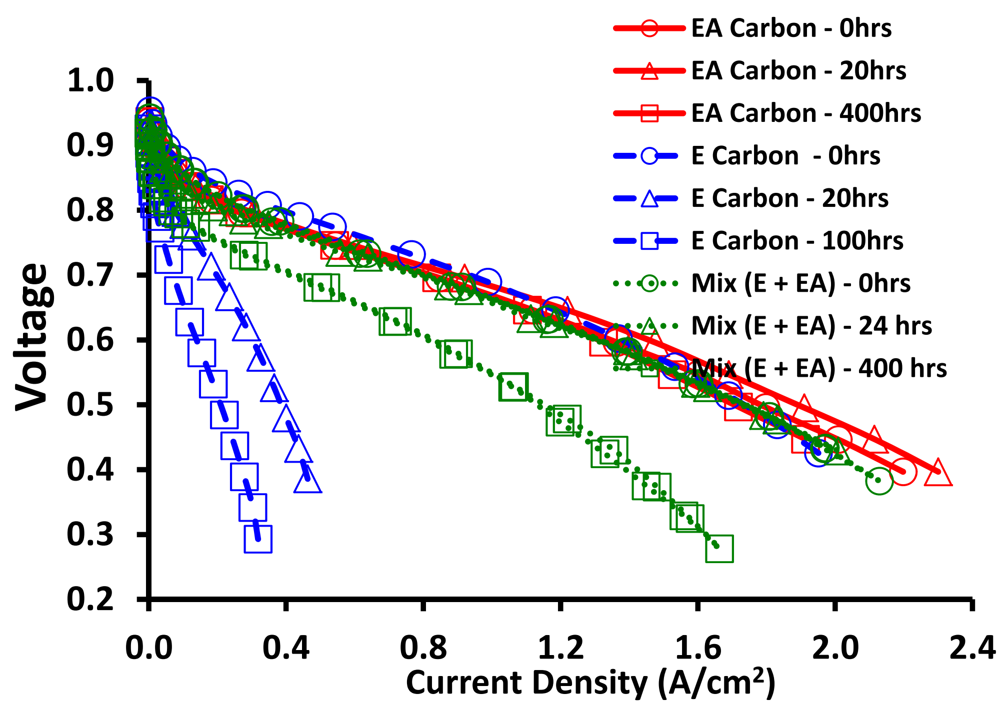
Note: MEA Pt loadings were: 0.15 mg/cm² (E) / 0.15 mg/cm² (Ea+E) / 0.25 mg/cm² (Ea)

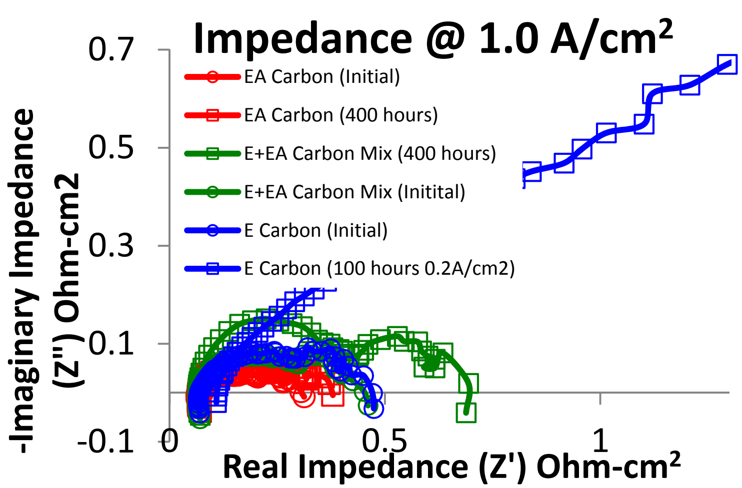
Mixed Catalysts (E + Ea) – Fresh vs. Carbon AST

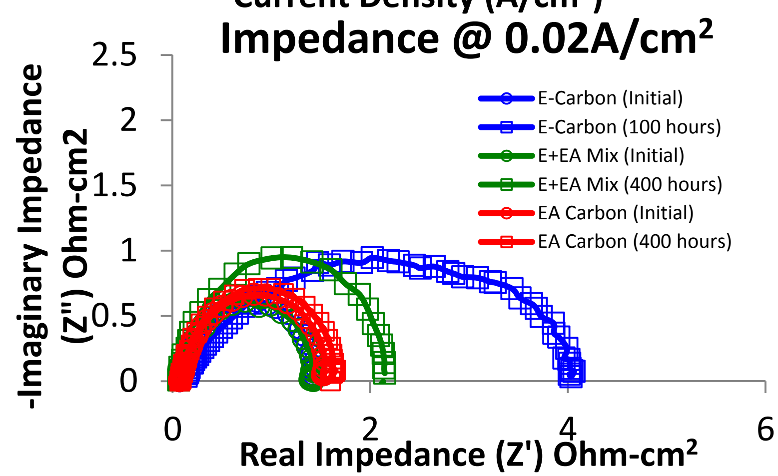


Comparison of Carbon Corrosion – Potential Mitigation of Transport Losses → Mixing Stable Materials to Keep CL Structure





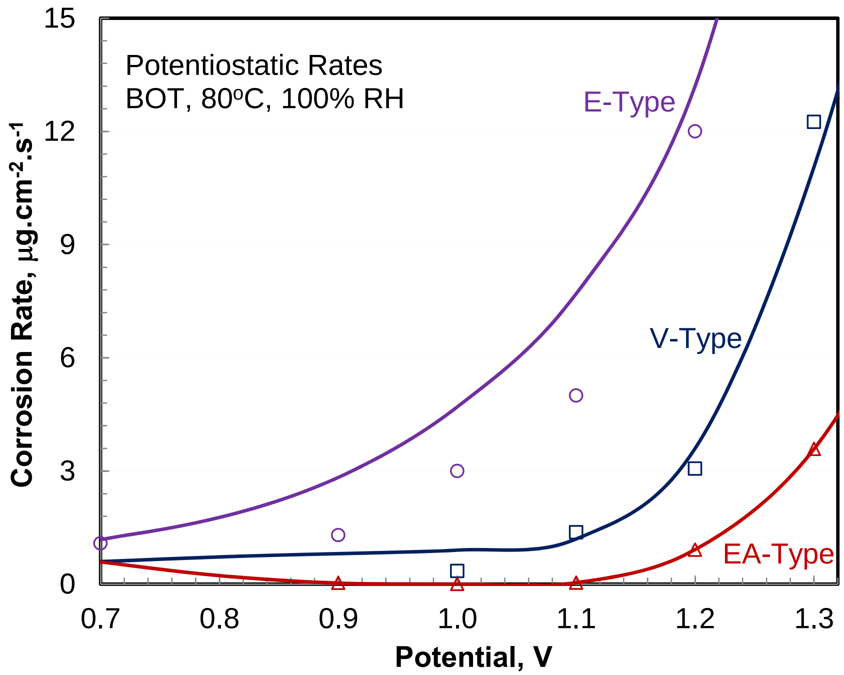


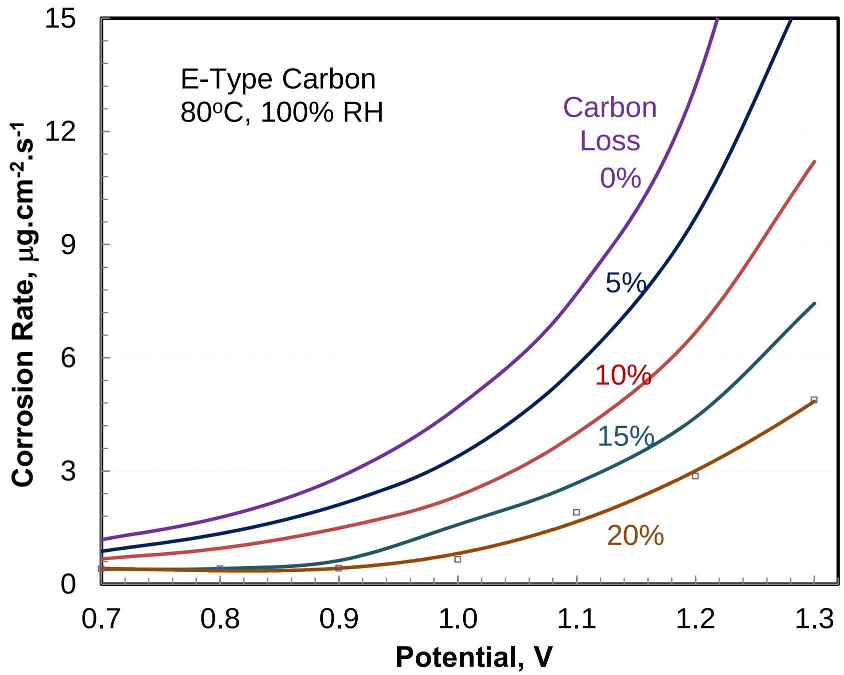


Note: MEA Pt loadings were: 0.15 mg/cm² (E) / 0.15 mg/cm² (Ea+E) / 0.25 mg/cm² (Ea)

Modeling of Carbon Corrosion Kinetics

- E-Type carbon corrodes ~4X faster than V-Type carbon
- E-Type carbon corrodes ~7X faster than EA-Type carbon
    - Corrosion Rate E > V > EA (Potentiostatic: 1.2 V, 80°C and 100% RH).
  - Corrosion rate of E-Type carbon slows down with ageing
  - Corrosion rates of V-Type and EA-Type carbons show smaller effects of ageing
- Hysteresis in corrosion rates under cyclic potentials – created by oxidation reduction cycles (adsorbed oxygen species)





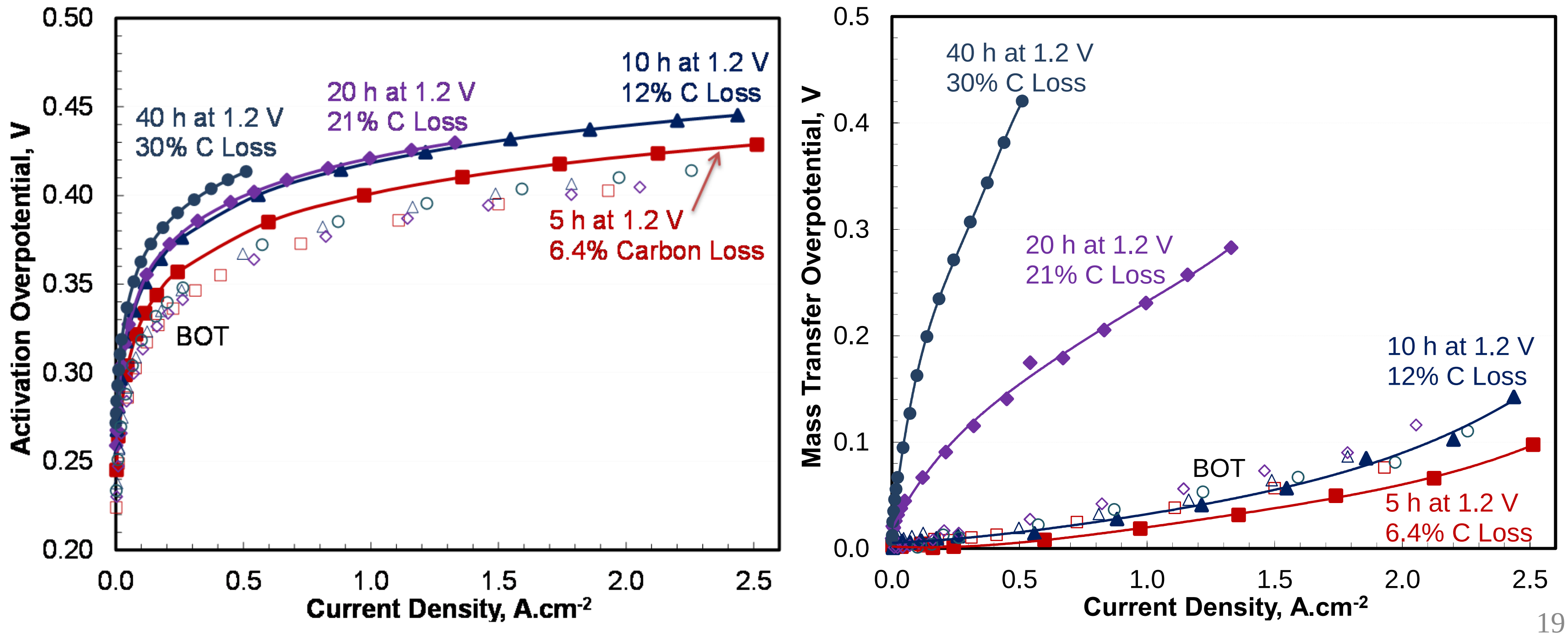
Breakdown of Overpotentials

Carbon loss <10%

- Performance degradation with ageing is primarily due to the increase in activation for current densities <1 A/cm^2
- At higher current densities, increased activation and mass transfer overpotentials contribute equally to performance degradation

Carbon loss >20%

- Performance degradation dominated by increase in mass transfer overpotentials even at lower current densities
- Radical changes in electrode structure



Summary

- **ElectrodE Layer Degradation**
  - Kinetic and Mass Transport effects
    - Carbon loss <10%
      - Performance degradation with ageing is primarily due to the increase in activation for current densities <1 A/cm^2
    - Carbon loss >20%
      - Performance degradation dominated by increase in mass transfer overpotentials even at lower current densities

- **Microstructural changes**
  - "localized bands" of Carbon corrosion observed (primarily for HSAC)
    - Preferential oxidation of E-carbon forming bands of dense "graphite-oxide" encapsulating large Pt nanoparticles
  - EA-carbon shows ~ no oxidation, retaining its graphitic structure
  - Pt particle size changes are significant for E-carbon and little for EA-carbon.
  - **Ea mixed with E maintains pore structure of CL – maintains transport**

Thanks to

- U.S. DOE -EERE Fuel Cell Technologies Program for financial support of this work
  - Technology Development Manager: Nancy Garland

Other Acknowledgments:

- Other materials provided by:
    - **Ion Power**
    - **SGL Carbon**
    - **W.L. Gore**
    - **Tanaka**
    - **DuPont**

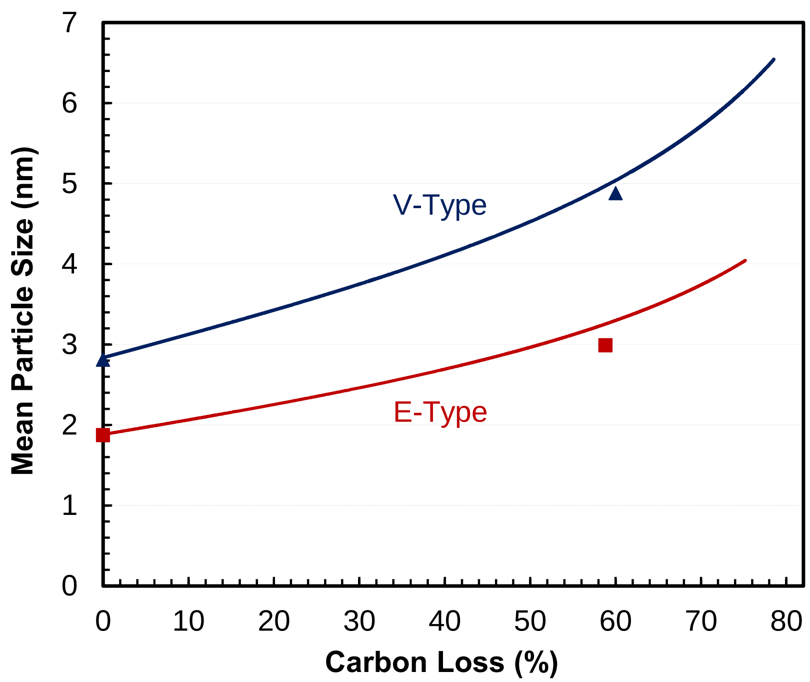
Future Work

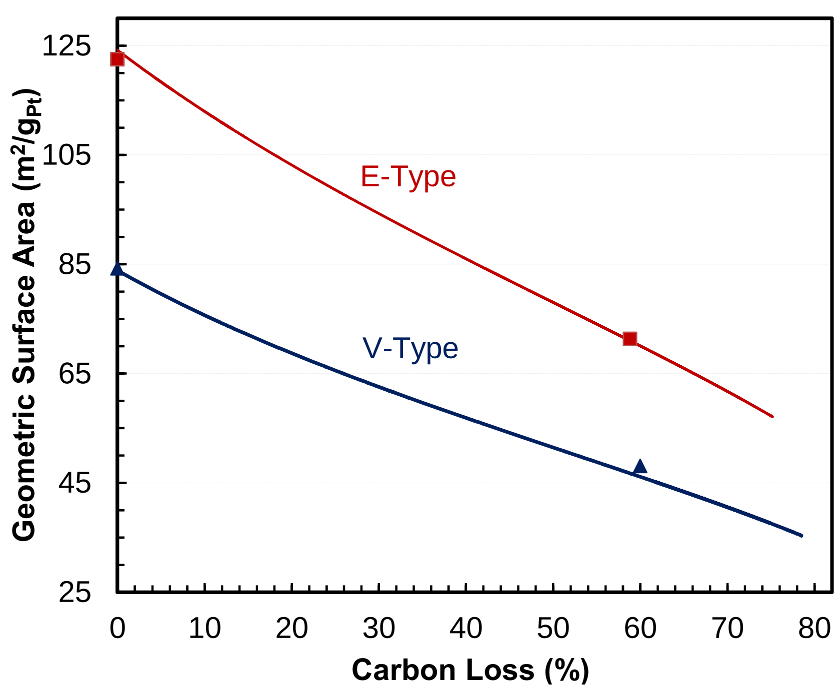
- **Define effect of carbon corrosion on CL structure and transport losses**
  - Further quantitate relationship between carbon corrosion and resulting changes in CCL structure (Pt/pore distributions, Pt utilization, ECSA)
    - Quantification of E vs. Ea carbon structures and mixed formulations
    - Quantitate and compare the loss of pore volume after testing a sequence of times drive cycle tests of 0, 50, 100, 200, 400, 1000 hours
    - Complete testing comparison of single type carbons and mixed carbon (HSAC and graphitized) comparing the structure effect on mass transport losses
    - Correlate microstructural/compositional observations with AST protocols and fuel cell testing
- **Understand MEA structure and durability effects**
  - **Carbon/Nafion/Catalyst**
  - Understand structure of catalyst layer effect on durability; different methods of forming catalyst layers
  - Evaluate the effect of catalyst layer cracks on membrane durability during wet/dry drive cycle tests, and define crack width/depth required to induce enhanced degradation
  - Improve durability/performance of low loaded MEAs (0.05 mg/cm^2)
  - Identify ionomer degradation source for FER (CL vs membrane)

Pt Particle Growth due to Carbon Corrosion

Pt particle growth includes Pt coalescence due to carbon loss

- Rate constant for coalescence derived from BOT and EOT PSD
- Measured ECSA loss >> decrease in GSA because of growth of Pt particles





Performance Loss due to Carbon Corrosion

Four cells with E-Type carbon support subjected to B2 AST for 5-40 h

- ECSA loss exceeded 40% after 10 h at 1.2 V: 12% carbon loss, 36 mV drop in cell voltage at 1 A/cm^2
- Decrease in mass activity correlates with reduction in ECSA

Effect of carbon corrosion on ORR kinetic parameters

- Tafel slope was nearly constant (74.5 mV/dec) for <10% carbon loss: $\alpha = 0.47$ for n = 2
- Increase in Tafel slope for higher carbon loss may indicate change in ORR rate limiting step